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Synthesis and High Temperature Chemistry of Methylsilsesquioxane  
Polymers Produced by Titanium Catalyzed Redistribution of  
Methylhydrido-oligo- and polysiloxanes.

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by

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**Synthesis and High Temperature Chemistry of  
Methylsilsesquioxane Polymers Produced by Titanium Catalyzed  
Redistribution of Methylhydridooligo- and polysiloxanes.**

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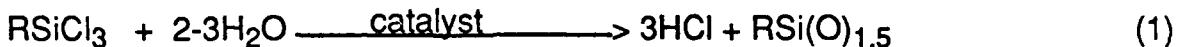
**Abstract**

The synthetic utility of homogeneous titanium catalyzed redistribution of the cyclomers  $-\text{[MeHSiO]}_x$  (where  $x = 4$  or  $5$ ) and the linear oligomer  $-\text{[MeHSiO]}_n$  ( $M_n \approx 2,200$  D) was explored as a route to  $\text{MeSiH}_3$  and a methylsilsesquioxane-methylhydridopolysiloxane copolymer of approximate composition  $-\text{[MeHSiO]}_{0.35}[\text{MeSi(O)}_{1.5}]_{0.65}-$ . The high temperature behavior of the titanium derived methylsilsesquioxane copolymer follows closely that of similar polymers prepared by sol-gel processing. Heating under nitrogen to  $800$ - $1000^\circ\text{C}$  at a heating rate of  $5^\circ\text{C}/\text{min}$  gives a black glass with an apparent composition of:  $\text{SiO}_2$  (70%);  $\text{SiC}$  (19%) and  $\text{C}$  (10%). The apparent composition belies the true nature of the material which is probably a metastable glass, best described by the various Si-X bonding arrangements (X = O, C, H). Thus, MAS NMR and DRIFT spectroscopy show the existence of species containing 4, 3 and 2 Si-O bonds with the remaining bonds being either Si-C or Si-H. At  $600^\circ\text{C}$  and below (under  $\text{N}_2$ ), the Si-C bonds are almost exclusively  $\text{Si-CH}_3$ , which is an indication of the extraordinary thermal stability of silsesquioxane polymers. Above  $600^\circ\text{C}$ , the  $\text{CH}_3$  groups react with Si-O bonds to generate Si-OH bonds, new Si-C bonds and Si-H bonds. This type of reactivity is illustrative of the basic chemistry involved in the carbothermal reduction of  $\text{SiO}_2$  to Si and/or  $\text{SiC}$  as well as the degradation mechanisms of the polymer.

Heating the polymers in  $\text{O}_2$  gives ceramic yields of  $> 90\%$ . The product is primarily  $\text{SiO}_2$ . The evidence suggests that it is possible to prepare silica glasses using silsesquioxanes as precursors. Thus, silsesquioxanes may offer an alternative to sol-gel processing methods for processing silica.

## Introduction

Silsesquioxanes,  $[\text{RSi(O)}_{1.5}]_n$ , have recently been explored as models for silica surfaces<sup>1</sup> and particles,<sup>2</sup> as precursors (in the presence of  $\text{NH}_3$ ) for the synthesis of nitrided glasses<sup>3</sup> and silicon oxynitride ( $\text{Si}_2\text{ON}_2$ ),<sup>4</sup> as precursors for silicon carbide powders<sup>5</sup> and, silicon carbide containing (black) glasses especially as a matrix for carbon fibers,<sup>6,7</sup> and, as photoresists.<sup>8</sup> The typical synthesis involves the hydrolysis of the corresponding silyl chloride,  $\text{RSiCl}_3$ , in the presence of a catalyst (acid or base) in an appropriate organic solvent.<sup>9</sup>



Although represented by  $\text{RSi(O)}_{1.5}$ , the products of reaction (1) are normally a mixture of polyhedral oligosilsesquioxanes,  $[\text{RSi(O)}_{1.5}]_x$  (generally < 40% yield) where  $x = 6, 8, 10$  etc., and polymeric species that contain silsesquioxane units and uncondensed silanols, e.g.

$-[\text{RSi(O)}_{1.5}]_x[\text{RSi(O)}_{0.5}(\text{OH})_2]_y[\text{RSi(O)}(\text{OH})]_z-$ .<sup>9</sup> Heating the latter species to 200-400°C, especially in the presence of catalytic amounts of base, results in the elimination of volatile polyhedral oligosilsesquioxanes,  $\text{H}_2\text{O}$  and the formation of ladder and/or polyhedral polysilsesquioxanes.

The synthesis of polysilsesquioxanes is of interest to us for a number of reasons. First, alkyl- and arylsilsesquioxanes are uncommonly stable in air at quite high temperatures with  $[\text{MeSi(O)}_{1.5}]_8$  stable to  $\approx 400^\circ\text{C}$ ,  $[\text{PhSi(O)}_{1.5}]_8$  stable to 500°C and the polyphenylsilsesquioxanes stable to temperatures of 600°C.<sup>9</sup> Thus, these inorganic polymers represent a potential alternative to organic polymers for a wide variety of high temperature applications, providing useful synthetic routes can be developed that permit the development of tractable polysilsesquioxanes.

Second, the synthesis of poly-3-tolylsilsesquioxanes results in the formation of mesomorphic lamellar microstructures which points the way toward wholly inorganic liquid crystalline materials. Again, this assumes that useful synthetic routes to tractable materials can be developed.

Third, methylsilsesquioxane,  $[\text{MeSi(O)}_{1.5}]$ , is the oxygen analog of methylsilsesquiazane,  $[\text{MeSi(NH)}_{1.5}]_x$ , a type of monomer unit that forms in the synthesis of polysilazane preceramic polymers. Thus, studies of the high temperature chemistry of  $[\text{MeSi(O)}_{1.5}]_x$  should provide useful comparisons with the analogous chemistry of Si-methylpolysilazane

preceramics.

Finally, one of us has recently shown that a titanium catalyst derived from  $Cp_2TiMe_2$  is extremely effective for the room temperature redistribution of hydridosiloxanes as illustrated by reaction (2):<sup>10</sup>



Thus, studies of this reaction pertain to our continuing interest in the development of catalytic routes to inorganic polymers.<sup>11</sup>

We report here on the use of the same type of system for the catalytic redistribution of methylhydridopolysiloxanes,  $-\text{[MeHSiO]}_x-$ , as exemplified by reaction (3), for the synthesis of polysilsesquioxanes and studies of the



high temperature chemistry of the resultant polymer. The long term objectives that have guided the studies presented below are based both on the above cited interests; on the potential utility of polysilsesquioxanes as an alternate route to sol-gel processing for the synthesis of silica glasses; and, on the fact that we have recently extended reaction (3) to the polymerization of the oligosilazanes  $-\text{[MeHSiNH]}_x-$  and  $-\text{[H}_2\text{SiNMe]}_x-$ .<sup>12</sup>

## Experimental

**General.** The polysiloxanes,  $-\text{[MeHSiO]}_4-$ ,  $-\text{[MeHSiO]}_5-$ , and  $-\text{[MeHSiO]}_x-$  ( $M_n \approx 2,200$ ) were purchased from Petrarch Systems. The cyclomers were distilled under  $N_2$  and stored under  $N_2$  prior to use. The polymer was stored over  $CaH_2$ , under  $N_2$  prior to use.  $Cp_2TiCl_2$ ,  $CpTiCl_3$  and  $Ti(NMe_2)_4$  were purchased from Strem Chemicals and used as received.  $NaBH_4$  and  $MeLi$  were purchased from Alfa Chemicals and used as received.  $Cp_2TiMe_2$ ,  $CpTiMe_3$  and  $Cp_2TiBH_4$  were prepared as described in the literature.<sup>13-15</sup> Elemental analyses were performed by Galbraith Laboratories.

**Standard Catalytic Run.** An oven dried, 40 mL pop-bottle glass reactor, containing a stir bar and 5 mg of catalyst was sealed under nitrogen. Alternately, 5 mg of catalyst was dissolved in 100  $\mu\text{L}$  of hexane and added by syringe.  $Ti(NMe_2)_4$  was also added by syringe. 3 mL of the methylhydridosiloxane were injected through the septum and the reaction was stirred. Reaction progress was followed qualitatively by noting onset

of catalysis typically indicated by the formation of an intense royal blue color and, by noting the time required for complete crosslinking (gelation).

**Standard Pyrolysis Run.** Bulk pyrolyses were run to obtain ceramic samples for analytical purposes or for the DRIFT spectra. These pyrolyses were run in a Lindberg furnace (Model No. 58114, single zone) equipped with a Eurotherm temperature controller (Model no. 818S). A 5.00 cm O. D. (4.44 cm I.D.) mullite tube, cooled at both ends by means of water circulated through copper coils, was inserted into the furnace to protect the heating coils and for even heat distribution. The tube could be sealed at both ends using stainless steel caps and viton o-rings. One cap was fitted with gas inlet and outlet ports to control both the pyrolysis atmosphere and the gas flow rates. Alternately, pyrolyses were conducted in a 3.8 cm O.D. x 45.7 cm quartz tube, sealed at one end via a quartz cap with a standard o-ring seal. The cap was fitted with gas inlet and outlet ports. The quartz tube was inserted into the mullite tube. This tube was designed for transport of samples in and out of a dry-box.

Half-cylinder stainless steel pyrolysis boats containing weighed amounts of crosslinked polymer precursor were placed in the quartz tube under the desired atmosphere. The quartz tube with sample was then inserted into the mullite tube so that the samples were in the center of the heated zone (approximately 12 cm in length, usually only 2 or 3 samples fit in this region). The samples were then pyrolyzed by heating, under the desired atmosphere ( $N_2$  or synthetic air), at 5°C/min to 800 or 1000°C. The standard gas flow rate was 0.25 m<sup>3</sup>/hr. Sample sizes were typically 200-800 mg. Sample preparation involved placing the crosslinked polymer under vacuum for 2 hr to remove  $MeSiH_3$  and hexane.

Weight loss experiments, to obtain ceramic yields, were conducted using a Perkin Elmer TGA-7. 20-40 mg samples, prepared as above, were placed in the platinum pyrolysis boat in  $N_2$  or synthetic air and heated at 5°C/min to 800°C.

**NMR Studies.** Spectra were recorded on an MSL 400 Brüker spectrometer at 79.5, 100.6 and 400 MHz for <sup>13</sup>C, <sup>29</sup>Si and <sup>1</sup>H respectively. The spinning rate was 4 kHz. For the <sup>29</sup>Si and <sup>1</sup>H MAS experiments, pulsed widths of 2.5  $\mu$ s and 6  $\mu$ s respectively were used with delays between pulses of 60 s and 4 s. For the CP MAS experiments, contact time of 2 ms was used for <sup>29</sup>Si and 1 ms for <sup>1</sup>H. Tetramethylsilane was used as reference for all the NMR data. Sample sizes for all spectra were typically  $\approx$  500 mg.

## Results and Discussion

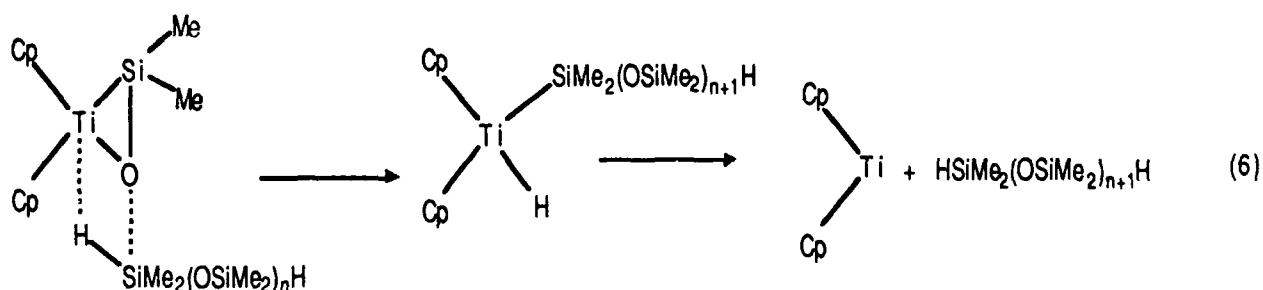
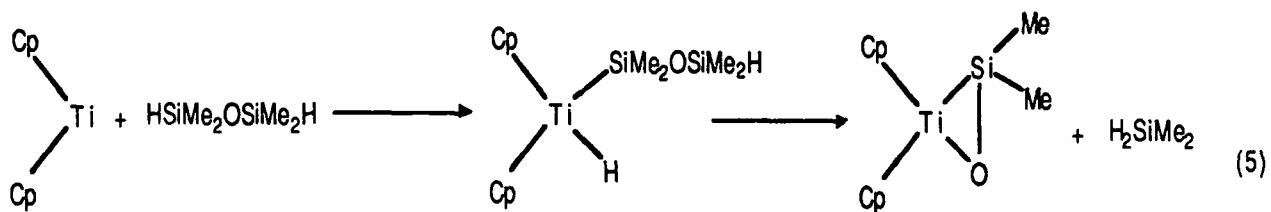
The synthetic objectives of the work presented here have focussed on optimizing the rate and extent of crosslinking in reaction (3) as a means of minimizing reaction time and maximizing ceramic yield. Thus, we briefly examined the effects of some simple modifications to the titanium center and changes in the type of  $-\text{[MeHSiO}]_x-$  precursor on reaction rate.

Studies dedicated to the elucidation of the kinetics and mechanisms of reaction are ongoing and will be presented in detail elsewhere.<sup>16</sup> However, it is reasonable to discuss briefly two possible mechanism(s) whereby the royal blue, Ti (III) catalyst that derives from  $\text{Cp}_2\text{TiMe}_2$  promotes rapid redistribution of  $-\text{[MeHSiO}]_x-$  cyclomers and oligomers to  $-\text{[MeSi(O}]_{1.5}]_x-$ .

Catalytic redistribution of hydridosiloxanes, e.g.  $(\text{HSiMe}_2)_2\text{O}$ , by noble metals was first reported by Curtis et al over a decade ago.<sup>17</sup>  $\text{Cp}_2\text{TiMe}_2$  will also catalyze the redistribution of  $(\text{HSiMe}_2)_2\text{O}$ , reaction (4):<sup>10,16</sup>

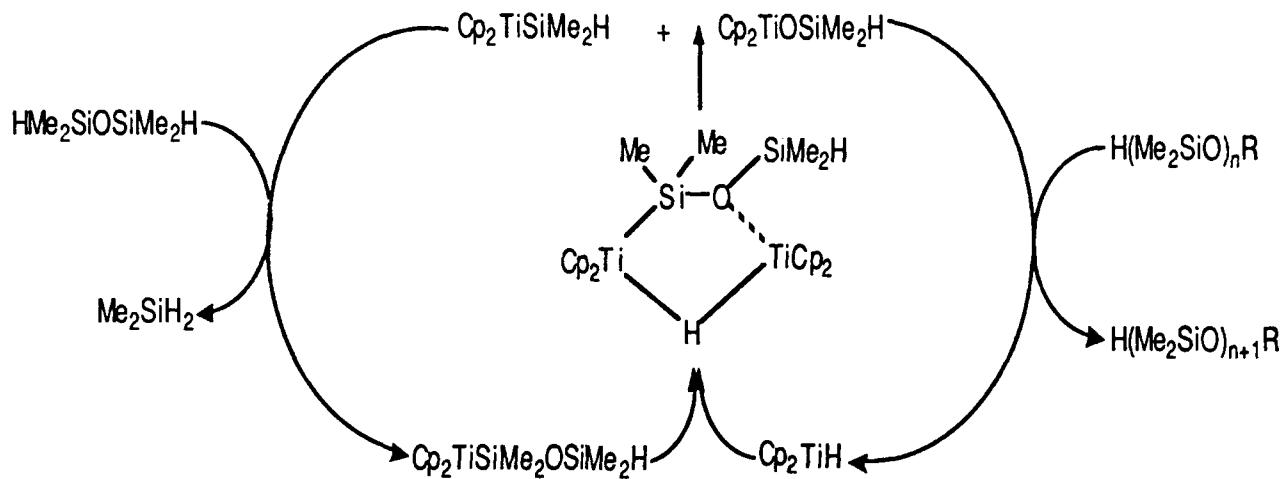


The mechanism proposed by Curtis et al offers a useful starting point for developing a mechanism for titanium catalyzed redistribution of hydridosiloxanes. Scheme 1 illustrates a potential mechanism for titanium catalyzed polymerization of  $\text{H}(\text{Me}_2\text{Si})_2\text{O}$ , based on the intermediacy titanocene and Ti(IV) species.<sup>10</sup>



Scheme 1

Scheme 2 offers an alternate mechanism based on a dinuclear, Ti(III) species:



Scheme 2

Despite these proposed mechanisms, there are still several questions that remain as to the nature of the true active species as will become apparent in the next section.

#### Catalysis Studies.

The relative reactivities and extent of crosslinking of the cyclotetramer,  $(-\text{[MeHSiO}]_4-)$ , the cyclopentamer  $(-\text{[MeHSiO}]_5-)$ , and the linear oligomer,  $-\text{[MeHSiO}]_x-$  were established using a standard set of reaction conditions (see experimental), and  $\text{Cp}_2\text{TiMe}_2$  as the catalyst precursor. The results of these studies are shown in Table 1.

#### Insert Table 1

Full crosslinking of the cyclomers is considerably slower than for the long chain oligomer. The most likely explanation is that cleavage of an Si-O bond is a necessary prelude to redistribution and Si-O bond cleavage in rings is slower than it is in straight chain oligomers. This seems likely for two reasons. First, polymerization and redistribution of the cyclotetramer is slower than the cyclopentamer which might be expected based on its

smaller ring size and consequent greater stability. Second, the final polymers are essentially identical in terms of chemical analysis (see Table 2) and the extent of crosslinking.

### Insert Table 2

We can estimate, qualitatively, the extent of crosslinking for all three polymers by the ceramic yield (Table 1), if we assume that unreacted precursor and poorly crosslinked segments are likely to volatilize during pyrolysis under nitrogen. The ceramic yields (76-80%) of all three polymers are, within the error limits of the 900°C TGA results, identical. Therefore, the extent of the crosslinking for all three polymers is identical. This suggests that once ring opening of the tetra- and pentacyclomer have occurred, the same chemical species or intermediates participate in the redistribution reaction and give the same crosslinked polymer.

In the next set of studies, we conducted a simple catalyst survey again using a standard set of reaction conditions, with the oligomer as substrate. We examined the utility of the titanium complexes:  $Ti(NMe_2)_4$ ,  $Ti(NEt_2)_4$ ,  $Cp_2Ti(NEt_2)_2$ ,  $Cp_2TiMe_2$ ,  $CpTiMe_3$  and,  $Cp_2TiBH_4$  as catalyst precursors. These complexes were chosen because they are easily synthesized via literature procedures or are available commercially. The results of this survey are recorded in Table 3.

### Insert Table 3

Of the catalysts tested, the original catalyst,  $Cp_2TiMe_2$ , provides the best results despite the high activity of  $CpTiMe_3$ . This is because  $CpTiMe_3$  is not stable at room temperature and is even difficult to handle at 0°C. The  $Cp_2TiMe_2$  catalyst precursor is also unstable and turns black even when stored under  $N_2$  and at -20°C by what is probably an autocatalytic decomposition process. This decomposition process also appears to occur in solution during initiation of the polymerization reactions. There is always an induction period prior to the appearance of the active, royal blue catalyst. This induction period is not entirely reproducible for the same reaction despite the use of freshly prepared, recrystallized  $Cp_2TiMe_2$ .

The fact that both  $Ti(NMe_2)_4$  and  $CpTiMe_3$  also catalyze reaction (3) suggests two possibilities. One is that two cyclopentadienyl ligands per

metal is not a necessary condition for catalysis of reaction (3); especially, given that the activity of  $CpTiMe_3$  is greater than that of  $Cp_2TiMe_2$ . A second possibility is that there are other mechanisms for catalyzing redistribution. In fact, base catalyzed redistribution of hydridosiloxanes is a well known phenomenon and has even been used to prepare  $-[MeSi(O)_{1.5}]_x$ .<sup>9</sup> Indeed,  $Ti(NMe_2)_4$  can be viewed as a strong base and might actually function as such. The catalyst solutions formed from  $Ti(NMe_2)_4$  are typically brown/black and appear to contain colloidal material. However, because all the catalysts tested were less useful than the original  $Cp_2TiMe_2$ , no further effort was made to elucidate the mechanisms of their reactions.

#### High Temperature Studies.

The high temperature studies described here were conducted primarily: (1) to develop an understanding of the stability of the  $-[MeHSiO]_x$ - polymers produced via reaction (3); (2) to identify modes of decomposition for comparison with the decomposition patterns of  $-[MeHSiNH]_x$ - and  $-H_2SiNMe]_x$ - and, to detail the chemical transformations that the polymer undergoes during heating to temperatures up to and including 1000 °C for comparison with previous studies on the pyrolysis of sol-gel derived  $-[MeSi(O)_{1.5}]_x$ - polymers.<sup>5</sup>

To begin with, it was necessary to identify a "standard" polymer for use in the high temperature studies. For the purposes of the present study we chose the polymer resulting from polymerization of  $H-[MeHSiO]_x-H$  (Mn = 2000) as the standard material. As noted above, the crosslinked polymers from each precursor methylhydridosiloxane are identical within the error limits of the methods of analysis. However, the combustion analyses (Table 2) do not correspond to the value calculated for  $-[MeSi(O)_{1.5}]_x$ - which assumes complete redistribution. The fact that the system does not attain complete redistribution is to be expected. As the degree of crosslinking increases, the mobility of the catalyst in the polymer decreases significantly and the concentration of reactive monomer units,  $-[MeHSiO]-$ , available for crosslinking and redistribution decreases accordingly. Therefore, the reaction must slow and eventually stop short of complete reaction. Fortunately, it stops in essentially the same place for all of the precursors used.

Because the oligomer is easy to handle and reacts most rapidly, it was used as the initial precursor for all of the high temperature studies. The

fully polymerized form was further characterized by TGA (Figure 1), FTIR and NMR. Chemical analyses were performed for the polymer at room temperature and after heating to 900°C under nitrogen for one hour (Table 4). Diffuse reflectance infrared spectra (DRIFTS) were also taken both at room temperature and for the 200, 400, 600, 800, and 1000°C samples. The DRIFTS data are presented in Figure 2.  $^{29}\text{Si}$ ,  $^{13}\text{C}$  and proton magic angle spinning (MAS) and cross polarized (CP) NMR spectra were also recorded at each temperature. The proton spectra reveal very little, except the presence of Si-Me and Si-H at lower temperatures and, a small peak for Si-H plus a broadened peak for saturated C-H adjacent to Si at temperatures  $\geq 800^\circ\text{C}$ . The  $^{29}\text{Si}$  MAS and CP spectra and, the  $^{13}\text{C}$  spectra for the various temperatures are shown in Figures 3-5. Figure 6 shows the quantitative evolution of the various species based on the  $^{29}\text{Si}$  MAS spectra. The peaks in Figures 3 and 4 can be readily assigned to different silicon units based on literature values as listed in Table 5.<sup>18</sup>

#### **Insert Tables 4 and 5**

In the following sections, we discuss the chemical evolution of the polymer as it is heated to 1000°C using the data contained in Figures 1-6 and Tables 1-4.

#### **Insert Figures 1-6**

#### Room Temperature

The composition of the "standard" polymer precursor, based on the  $^{29}\text{Si}$ , is approximately  $[\text{MeSiO}_{1.5}]_{0.65}[\text{MeHSiO}]_{0.28}[\text{MeSi(OH)O}]_{0.04}[\text{Me}_3\text{SiO}]_{0.03}$ . The proton NMR also reveals the presence of Si-H groups at 4.5 ppm. The  $^{13}\text{C}$  spectrum shows two peaks at -2.9 and 1.1 ppm that can be assigned to the T and D<sup>H</sup> units respectively. The DRIFT spectrum confirms part of this assignment in that there is an obvious  $\nu$  Si-H peak at  $2200\text{ cm}^{-1}$ . In addition, the DRIFT spectrum reveals sharp  $\nu$  C-H peaks at  $2800\text{-}2950\text{ cm}^{-1}$  normal for Si-CH<sub>3</sub>. The presence of Me<sub>3</sub>SiO- and Si-OH moieties cannot be confirmed by DRIFTS because  $\nu$  C-H of the M group is lost in the  $\nu$  C-H of the T and D<sup>H</sup> units and  $\nu$  Si-OH ( $3200\text{-}3400\text{ cm}^{-1}$ ) is apparently lost in the background noise. However, the presence of both are expected given that one can only prepare a well defined ( $M_n \approx 2000$  D) oligomer of  $-[\text{MeHSiO}]_x-$  by ring opening polymerization of the cyclotrimer,  $-[\text{MeHSiO}]_3-$ , using Me<sub>3</sub>SiO-

and a water workup. It would be reasonable to confirm the above NMR determined composition by chemical analysis; however, the error limits for the analysis of preceramics are somewhat higher than for typical organic molecules and do not permit a reliable calculation.<sup>19</sup> All that can be said from the data presented in Table 2 is that the polymer composition does lie between those calculated for  $-[\text{MeHSiO}]_x-$  and  $-[\text{MeSi(O)}_{1.5}]_x-$ .

### 200°C

Heating the polymer to 200°C appears to have little effect on the DRIFTS or the NMR spectra. One might expect the Si-OH groups to condense with  $\text{Me}_3\text{SiO}^-$  groups or react with Si-H bonds to form Si-O-Si bonds and release either  $\text{Me}_3\text{Si-OH}$  or  $\text{H}_2$ . Although the dehydrocoupling reaction is possible, the concentration of both the Si-OH and the  $\text{Me}_3\text{SiO}$ -units are too low to expect significant condensation to occur. We do see some weight loss in the TGA at 200°C but this is more likely the result of depolymerization of  $-[\text{MeHSiO}]_x-$  segments as suggested by the slight diminution of  $\nu$  Si-H in the DRIFT spectrum relative to  $\nu$  C-H.

### 400°C

At this temperature, we begin to see elimination of Si-H bonds as witnessed by the significant loss of intensity of the  $\nu$  Si-H absorption in the DRIFTS. This must be due to loss by depolymerization of  $-[\text{MeHSiO}]_x-$  segments, reaction with Si-OH bonds and probably, some oxidation due to the presence of adventitious oxygen. The less sensitive  $^{29}\text{Si}$  MAS and  $^1\text{H}$  NMR spectra suggest that the 400°C sample is composed entirely of  $-[\text{MeSi(O)}_{1.5}]_x-$ . However, the use of cross polarization techniques (Figure 5) confirms the DRIFT spectrum revealing remnants of  $-[\text{MeHSiO}]$ - and a very small amount of  $-[\text{MeSi(OH)}\text{O}]$ - . The  $^{13}\text{C}$  spectrum has changed somewhat in that the peak at 1.1 ppm is reduced to a shoulder on the major peak which has shifted somewhat from -2.9 to -3.5 ppm. The TGA reveals a significant weight loss at this temperature, (10-15%) in line with what is expected based on the NMR and DRIFTS data and probably accounted for by the above suggested depolymerization. Furthermore, the DSC reveals an endothermic process also likely associated with a depolymerization process.

One of the more important observations that can be made about the 400°C material is that it consists primarily of methylsilsesquioxane groups and appears to be stable under the pyrolysis conditions used. This is not

unexpected given that  $[\text{MeSi(O)}_{1.5}]_8$  is stable to  $\approx 415^\circ\text{C}$ .

### 600°C

The transition between 400 and 600°C results in some chemical changes in the 400°C polymer structure as is expected based on what is known about  $[\text{MeSi(O)}_{1.5}]_8$ .<sup>9</sup> The  $^{29}\text{Si}$  spectrum reveals a decrease in the number of T units by approximately 65% coincident with the appearance of peaks for D-type  $[\text{MeSi(CH}_x\text{)O}]$  units (14%) and Q (20%) units. Given that the relative amounts of each are reasonably close, the most likely explanation is that these species arise directly because of redistribution of the T groups. Partial oxidation by adventitious oxygen could account for the slightly higher abundance of the Q groups. The  $^{13}\text{C}$  NMR spectrum shows some changes as the peak attributable to  $\text{Si-CH}_x$  species broadens, shifts to -4.2 ppm and becomes asymmetric. This is in keeping with the formation of new D-type units in the polymer matrix. In the DRIFT spectrum, the  $\nu \text{ C-H}$  absorptions are still fairly sharp although diminished compared to the  $\nu \text{ Si-O}$  absorptions. Neither, the DRIFT spectrum nor the NMR studies provide evidence for either Si-H or SiO-H bonds.

Although, the 600°C material has clearly reacted in part, the evidence still suggests that much of the 400°C structure is retained. We can conclude that the 600°C material still resembles a polymer rather than a glass or a ceramic. This conclusion is supported by the very drastic changes that occur in on further heating to 800°C.

### 800°C

At this temperature, all the analytical tools reveal major changes in the structure of the material. In the NMR spectra, all of the peaks broaden significantly. The presence of Q units becomes significant, the number of T units continues to decrease (42%). The most important observation is the reappearance of  $\text{D}^{\text{H}}$  units in the  $^{29}\text{Si}$  spectrum and in the  $^1\text{H}$  NMR spectrum (Si-H). The  $^{13}\text{C}$  spectrum provides limited information at this stage because the peak becomes extremely broad (typical of a disordered material) and shifts its center to 5 ppm. Cross polarization cannot be used to enhance the signal because the average number of protons that remain on carbon has dropped considerably as shown in the TGA in Figure 1.

The DRIFT spectrum confirms the reappearance of the Si-H bonds ( $\nu \text{ Si-H}$  at  $\approx 2180 \text{ cm}^{-1}$ ). In addition, the 800°C DRIFT spectrum exhibits

well developed absorptions for  $\nu$  SiO-H at  $\approx$  3200-3400  $\text{cm}^{-1}$ . These absorptions were readily confirmed by exposing a sample of the pyrolyzed material to  $\text{D}_2\text{O}$  overnight. Following exchange of D for H, the absorption at 3200-3400  $\text{cm}^{-1}$  is considerably diminished and new absorptions appear at 2200-2400  $\text{cm}^{-1}$  that correspond to  $\nu$  SiO-D.

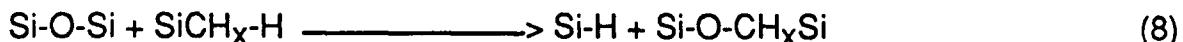
Four chemical changes occur on heating to 800°C (and probably at 600°C but to a lesser degree) that are related. Both Si-H and Si-OH units reappear and, Q and D-type or  $[\text{MeSi}(\text{CH}_x)\text{O}]$  units appear for the first time. Given that between approximately 400 and 800°C, the majority of the silicon containing units are the T units,  $\text{MeSi}(\text{O})_{1.5}$ , we can assume that they are responsible for the chemistry that ensues at or above 600°C.

To form new bonds, we must break either C-H, Si-C or Si-O bonds. To form Si-H and Si-OH bonds and new Si-C bonds (D units), we must break both C-H and Si-O bonds. Clearly, we must cleave Si-C bonds to make Q groups. What is not immediately evident is whether or not this cleavage occurs as a consequence of the formation of new Si-H and/or Si-OH bonds or after the fact.

To deconvolute the chemistry involved, one can begin by considering the formation of new Si-OH bonds from C-H and Si-O bonds. Using Occam's Razor, we assume that the simplest bond rearrangement process is as depicted in reaction (7):



The formation of Si-H bonds might be expected to arise from the opposite reaction, reaction (8):



At low temperatures, one might argue that thermodynamics would only permit an "either or" choice here. However, the chemistry observed occurs at 600-800°C where bond cleavage and bond forming processes often occur on a kinetic rather than on a thermodynamic basis. Even if reactions (7) and (8) are functional, it is likely that they are free radical processes.<sup>20</sup>

Reaction (7) would explain both the appearance of Si-OH species and D units. Reaction (8) provides a mechanism for the formation of Si-H units but leaves the question of the existence of species containing  $\text{Si-O-CH}_x\text{Si}$

linkages. Careful examination of the  $^{13}\text{C}$  NMR results at 400 and 600°C reveals the presence of small peaks in the 35-40 ppm range that provide support for the existence of  $\text{O}-\text{CH}_x\text{Si}$ . In addition, in the 800°C DRIFT spectrum, we see a sharp peak at  $1680\text{ cm}^{-1}$  indicative of a carbonyl group. A carbonyl group could only arise via the intermediacy of  $\text{O}-\text{CH}_x\text{Si}$ .

On prolonged heating, we would expect these species to evolve into  $\text{CO}$ , more  $\text{Si}-\text{H}$  bonds and possibly  $\text{Si}-\text{Si}$  bonds. We would also expect the  $\text{Si}-\text{CH}_x-\text{Si}$  linkages to lead to the formation of  $\text{SiC}$  based on the work of Yajima et al. In fact, Fox et al<sup>5</sup> report that heating methylsilsesquioxanes to temperatures of 1500°C does indeed lead to the formation of  $\text{SiC}$ .

The formation of Q groups is most difficult to explain. Above, we suggested that redistribution of T groups leads to the formation of Q groups and D groups; however, at the higher temperatures we observe the formation of a disproportionate amount of Q groups relative to D groups. Thus, additional mechanistic explanations are required. The bulk analyses of the materials at 900°C (Table 4) are essentially identical to those at 800°C. These analyses show that the relative proportion of carbon to silicon has changed from 1:1 in the starting material to 0.8 : 1.0 in the final glassy product. Consequently, during pyrolysis, 20% of the carbon groups have been lost to volatile products. We assume that less oxygen is lost by volatilization and this partially accounts for the high proportion of Q groups.

On a mechanistic level, the formation of  $[\text{MeSi}(\text{OH})\text{O}]$  units offers at least two suitable pathways for loss of carbon without oxygen. First,  $\beta$ -elimination of  $\text{CH}_4$  from one of these groups would lead to the intermediacy of silanone ( $\text{Si}=\text{O}$ ) units that would certainly react with surrounding  $\text{Si}-\text{O}$  bonds to give Q groups. Alternately, nucleophilic attack of the  $\text{Si}-\text{OH}$  group on a neighboring  $\text{Si}-\text{Me}$  group could also lead to displacement of  $\text{CH}_4$  and the formation of Q groups. A third possibility exists wherein neighboring  $\text{Si}-\text{H}$  groups react with  $\text{Si}-\text{Me}$  leading to loss of and the formation of  $\text{Si}-\text{Si}$  bonds which subsequently react with  $\text{Si}-\text{OH}$  groups to form Q groups. Although this is possible, we think it is less likely on thermodynamic grounds.

One of the more important conclusions that can be made, based on the chemistry of polymethylsilsesquioxanes over the 400 to 800°C range, concerns the reactions that occur when  $-\text{CH}_3$  groups react and reduce  $\text{Si}-\text{O}-\text{Si}$  linkages. *This chemistry has direct bearing on the mechanistic processes whereby  $\text{SiO}_2$  undergoes carbothermal reduction to  $\text{Si}_{\text{met}}$  or  $\text{SiC}$*

when heated with coke or charcoal.<sup>21</sup>

### 1000°C

The DRIFTS and the <sup>29</sup>Si MAS NMR spectra show that this sample has essentially the same chemical organization as the 800°C material. The only significant difference is in the hydrogen content of the material as revealed by our inability to obtain good CP MAS <sup>29</sup>Si spectra.

The <sup>29</sup>Si MAS NMR spectrum suggests that the composition of this material is SiO<sub>4</sub> ( $\approx$  30%), and SiO<sub>3</sub>C ( $\approx$  40%) with some SiO<sub>2</sub>C<sub>2</sub> and SiO<sub>2</sub>CH units. While it is certain that these silicon units no longer deserve the labels: Q, T, D or D<sup>H</sup> respectively, typically used for polysiloxanes; we also strongly resist using the labels, silica, or oxycarbides. The reason is that, to label something an oxycarbide etc., one has to be able to make the bulk material and identify its particular physical properties (e.g. silicon oxynitride, Si<sub>2</sub>ON<sub>2</sub>). To our knowledge, this has yet to be done for silicon oxycarbides, nor is it likely to occur given the thermodynamic instability of materials containing atomically mixed silicon, carbon and oxygen.<sup>21</sup>

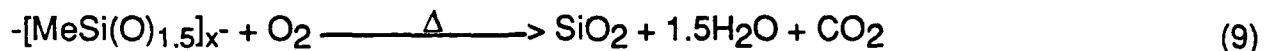
Furthermore, we and others have often relied on the use of the final chemical composition as a useful means of describing the ceramic products obtained from pyrolysis of a precursor. For example, Table 4 records the "apparent" ceramic composition for the 900°C pyrolysis products derived from the standard polymer. The apparent ceramic composition suggests the presence of SiC in the 900°C samples. Our spectroscopic studies do not give any clear indication in favor of the existence of SiC even at 1000°C. Consequently, we are inclined to conclude that SiC is not formed at these temperatures and can only form on heating to *much higher temperatures*--as found by Fox et al.<sup>5</sup> Moreover, we find that the "apparent" ceramic composition method of bookkeeping may be misleading if not properly presented.

At present, we would like to suggest that the materials formed on heating polymethylsilsesquioxanes to temperatures in the range of 600-1000 +°C are at best metastable glasses (or solid solutions). These glasses may, on extended heating in the same temperature range or heating to higher temperatures, form known ceramic materials. We will explore this concept again in another paper that focusses on the high temperature chemistry of polymethylsilazanes.

### Comparison with Sol-Gel Derived Polymethylsilsesquioxanes

Pyrolysis of the crosslinked polymers of Table 1 in nitrogen to 900°C permits us to compare our polymethylsilsesquioxane with the one prepared by Fox et al.<sup>5</sup> We find, as does Fox et al, that pyrolysis produces a "black glass". The compositions of the 900°C materials produced in both studies are listed in Table 5 with the apparent ceramic compositions. Within the error limits of the analytical technique, the compositions and the ceramic yields of the black glasses produced by both methods are very similar. The slight disparity in compositions can be attributed to the fact that the polymer precursors were not fully converted to  $-\text{[MeSi(O)}_{1.5}\text{]}_x-$ .

We have also examined the pyrolysis of the polymethylsilsesquioxane in an oxygen atmosphere to determine the effects of oxidation on the type of product obtained. As expected, the product is primarily  $\text{SiO}_2$  with some excess hydrogen and the ceramic yields for all the polymers are  $91 \pm 1\%$ . Calculated ceramic yields for reaction (4) are 90 %.



Consequently, we can conclude that the titanium catalyzed crosslinking and redistribution reactions of  $-\text{[MeHSiO]}_x-$  cyclomeric and oligomeric polysiloxanes lead to inorganic polymers almost identical with those produced by typical sol-gel processing. Moreover, pyrolysis of these preceramics leads to ceramic products essentially identical to those obtained by pyrolysis of the sol-gel processed material.

Future work in this area will examine the utility of titanium catalyzed redistribution for the synthesis of other silsesquioxanes.

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<u>Substrate</u>	<u>Reaction Time</u>	<u>Product Physical Characteristics</u>	<u>Ceramic<sup>a</sup> Yield (wt %)</u>
-[MeHSiO] <sub>4</sub> -	3-4 hr	Very Viscous in 1 hr Hard Plastic in 3-4 hr	78
-[MeHSiO] <sub>5</sub> -	15 min-1 hr	Hard Plastic	79
-[MeHSiO] <sub>x</sub> - $M_n \approx 2,200$ D	10-15 min	Hard Plastic	81

**Table 1. Polymerization of Methylhydridosiloxane Substrates by  $Cp_2TiMe_2$  at Room Temperature (21°C).** a. Ceramic yields were determined using thermogravimetric analysis. Heating rate was 5°C/min to 900°C in  $N_2$ . Reproducibility of the ceramic yields is  $\pm 5\%$ .

<u>Substrate</u>	<u>C</u>	<u>H</u>	<u>N</u>	<u>Si</u>	<u>O<sup>a,b</sup></u>	
-[MeHSiO] <sub>4</sub> -	19.45	5.62	0.00	43.60	31.33	
-[MeHSiO] <sub>5</sub> -	<b>20.37</b>	<b>5.98</b>	<b>0.00</b>	<b>45.11</b>	<b>28.54</b>	
-[MeHSiO] <sub>x</sub> - $M_n \approx 2,200$ D	17.93	4.45	0.11	40.66	28.82	
-[MeSi(O) <sub>1.5</sub> ] <sub>x</sub> -	17.90	4.50	---	41.84	35.76	calc.
-[MeHSiO] <sub>x</sub> -	19.98	6.71	---	46.71	26.61	calc.

**Table 2. Combustion Analysis of -[MeSi(O)<sub>1.5</sub>]<sub>x</sub>-, Formed By Reaction of Siloxane Substrates With  $Cp_2TiMe_2$  at 21°C.** a. Oxygen is determined by difference. b. Combustion analyses for preceramics are less accurate than those obtained for organic compounds. Typical error ranges are C ( $\pm 1-1.5\%$ ), H ( $\pm 1\%$ ), N ( $\pm 1-1.5\%$ ), Si ( $\pm 3\%$ ).<sup>19</sup>

<u>Catalyst<sup>a</sup></u>	<u>Reaction Time</u>	<u>Product Physical Characteristics</u>	<u>Ceramic<sup>b</sup> Yield (wt %)</u>
none	--	clear liquid	2
Cp <sub>2</sub> TiMe <sub>2</sub>	5-15 min	Hard Plastic	78
CpTiMe <sub>3</sub>	1 hr (0°C)	Hard Plastic	69
Ti(NMe <sub>2</sub> ) <sub>4</sub>	5 days	Viscous Liquid	29

**Table 3. Polymerization of -[MeHSiO]<sub>x</sub>- (M<sub>n</sub> ≈ 2,200 D) by Titanium Catalysts at Room Temperature.** a. No catalysis was observed with: Ti(NEt<sub>2</sub>)<sub>4</sub>, Cp<sub>2</sub>Ti(NEt<sub>2</sub>)<sub>2</sub>, Cp<sub>2</sub>TiBH<sub>4</sub>, and [Cp<sub>2</sub>ZrMe(THF)]BF<sub>4</sub>. b. Ceramic yields (± 5%) were determined via TGA using heating rates of 5°C/min to 900°C in N<sub>2</sub>.

<u>Substrate</u>	<u>C<sup>a</sup></u>	<u>H</u>	<u>N</u>	<u>Si</u>	<u>O<sup>b</sup></u>	<u>Ceramic<sup>c,d</sup></u> <u>Composition</u>
-[MeHSiO] <sub>4</sub> -	16.35	0.73	0.14	45.71	37.07	SiO <sub>2</sub> = 70 % SiC = 19 % C = 11 %
-[MeHSiO] <sub>5</sub> -	16.43	0.96	0.04	45.00	37.57	SiO <sub>2</sub> = 70 % SiC = 21 % C = 9 %
-[MeHSiO] <sub>x</sub> - M <sub>n</sub> ≈ 2,200 D	15.87	1.18	0.05	46.08	36.82	SiO <sub>2</sub> = 69 % SiC = 20 % C = 10 %
MeSi(O) <sub>1.5</sub> <sup>e</sup>	14.3	-.-	-.-	43	--.--	

**Table 5. Combustion Analyses of the 900°C Pyrolysis Product of -[MeSi(O)<sub>1.5</sub>]<sub>x</sub>-, Derived From Various -[MeHSiO]<sub>x</sub>- Substrates.**

a. Combustion analyses for preceramics are less accurate than those obtained for organic compounds. Typical error ranges are C ( $\pm 1\%$ ), H ( $\pm 0.5\%$ ), N ( $\pm 1\%$ ), Si ( $\pm 3\%$ ). Titanium analyzed in representative samples gave an average value of 0.1%. b. Oxygen is determined by difference. c. Pyrolyses were conducted in N<sub>2</sub> at a heating rate of 5°C/min. d. Apparent ceramic composition was determined by using silicon as the limiting element. e. Results from Fox et al<sup>5</sup>

<u>Si Unit</u>		<u>Chemical Shift (ppm vs TMS)</u>
Me <sub>3</sub> SiO-	M	+6., +7
HMe <sub>2</sub> SiO-	MH	-5.7
HOMe <sub>2</sub> SiO-	MCH	-11.12
-[Me <sub>2</sub> SiO]-	D	-20.00
-[MeHSiO]-	DH	-35.37
-[MeSi(OH)O]-	DOH	-55.00
-[MeSi(O) <sub>1.5</sub> ]-	T	-65.67
-[HSi(O) <sub>1.5</sub> ]-	TH	-85.00
-[(O) <sub>0.5</sub> Si(O) <sub>1.5</sub> ]-	Q	-100.0 to -110.0

**Table 5. <sup>29</sup>Si Chemical Shifts for Common Si Units.**

## Captions for Figures 1-6

**Figure 1. Thermogravimetric Analysis of  $-\text{[MeHSiO}]_{.35}[\text{MeSi(O)}_{1.5}]_{.65}-$  as a Function of Temperature.** The TGA heating schedule was 5°C/min in nitrogen. Bulk samples for the analyses were heated in a similar manner.

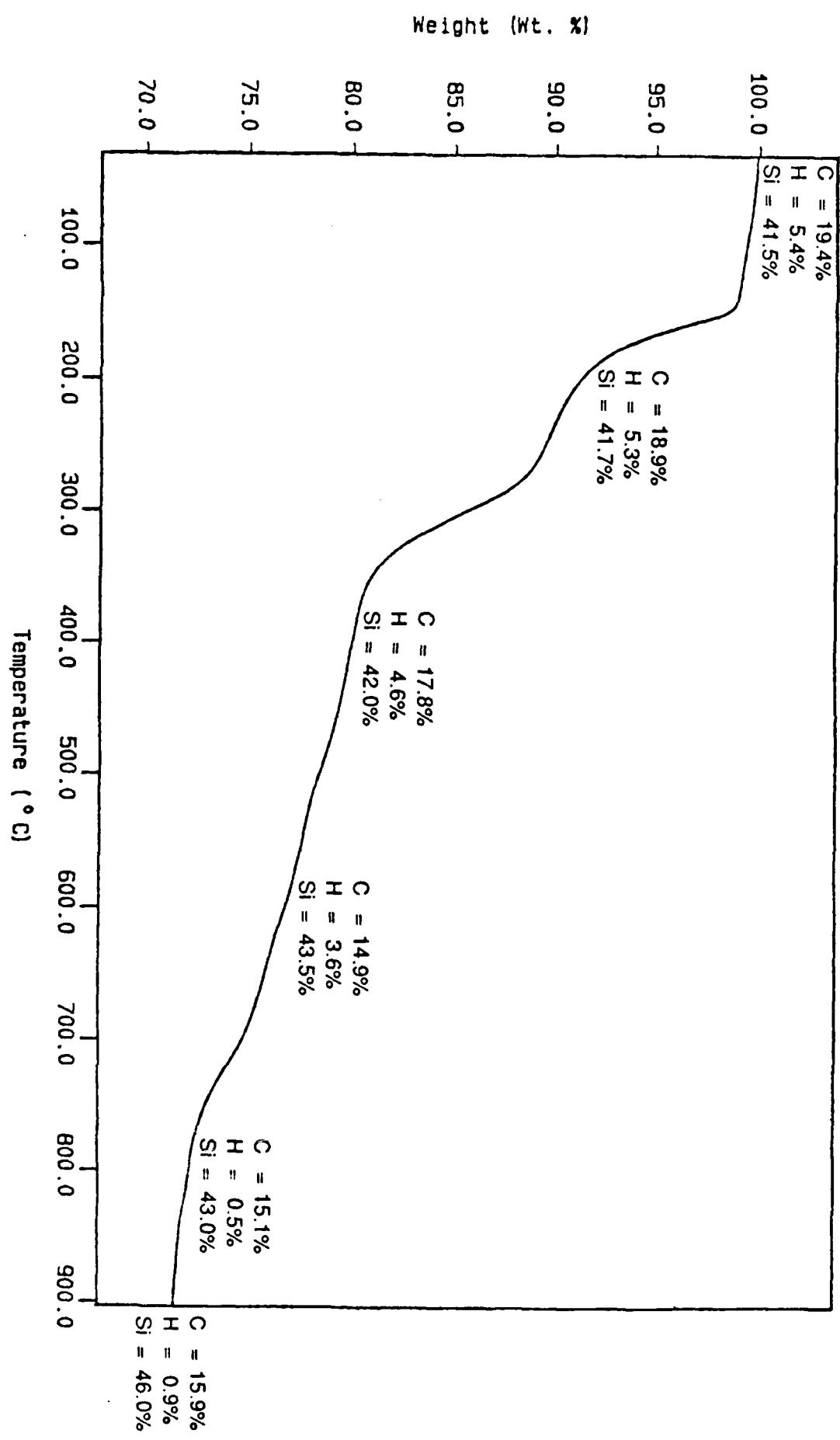
**Figure 2. Diffuse Reflectance Infrared Fourier Transform Spectra (DRIFTS) of  $-\text{[MeHSiO}]_{.35}[\text{MeSi(O)}_{1.5}]_{.65}-$  Following Heating to Selected Temperatures.** Samples were heated at 5°C/min in nitrogen to the desired temperature, mixed with KBr (under N<sub>2</sub>) and spectra taken under nitrogen.

**Figure 3. <sup>29</sup>Si MAS NMR Spectra of  $-\text{[MeHSiO}]_{.35}[\text{MeSi(O)}_{1.5}]_{.65}-$  Following Heating to Selected Temperatures.** Samples were heated at 5°C/min in nitrogen to the desired temperature and crushed under nitrogen and transferred to wide bore NMR tubes under dry box conditions.

**Figure 4. <sup>29</sup>Si CP MAS NMRs of  $-\text{[MeHSiO}]_{.35}[\text{MeSi(O)}_{1.5}]_{.65}-$  Following Heating to Selected Temperatures.** Samples were heated at 5°C/min in nitrogen to the desired temperature and crushed under nitrogen and transferred to wide bore NMR tubes under dry box conditions.

**Figure 5. <sup>13</sup>C CP MAS NMRs of  $-\text{[MeHSiO}]_{.35}[\text{MeSi(O)}_{1.5}]_{.65}-$  Following Heating to Selected Temperatures.** Samples were heated at 5°C/min in nitrogen to the desired temperature and crushed under nitrogen and transferred to wide bore NMR tubes under dry box conditions.

**Figure 6. Changes in Quantities of Various Silicon Species as a Function of Temperature.** Determined by <sup>29</sup>Si MAS NMR Spectra Following Heating of  $-\text{[MeHSiO}]_{.35}[\text{MeSi(O)}_{1.5}]_{.65}-$  to Selected Temperatures.



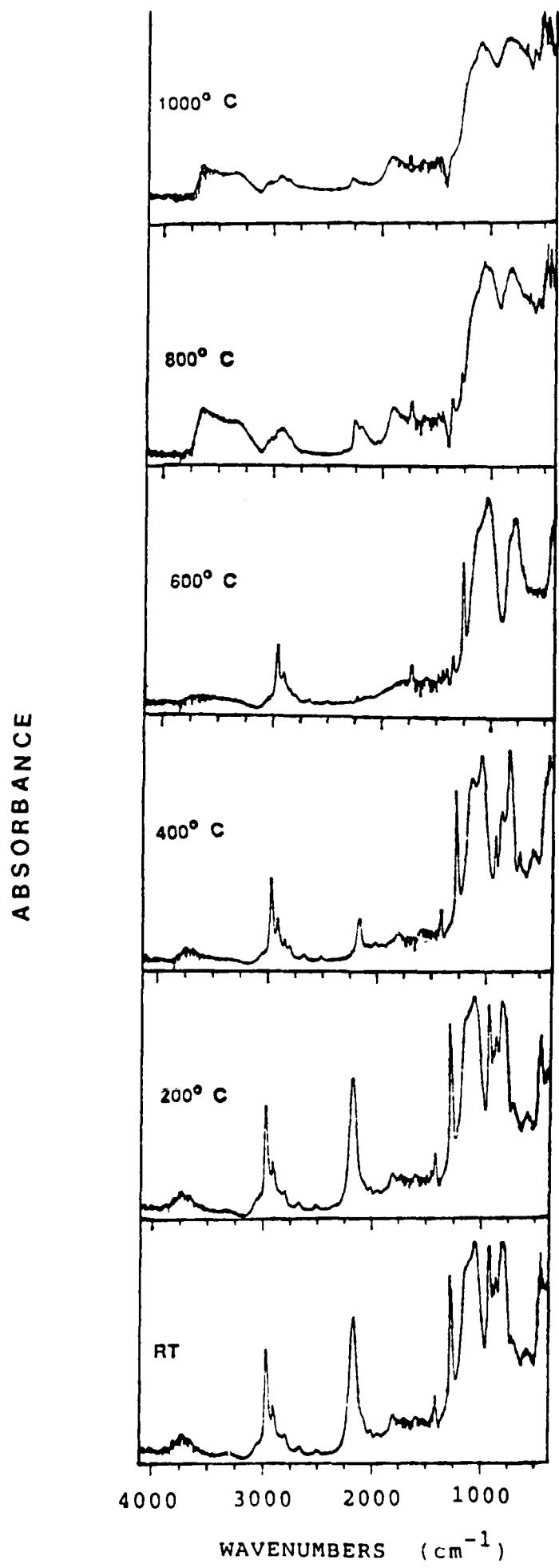


Fig. 2

The Chemical Evolution of  $-\text{[MeHSiO}]_{0.3}[\text{MeSi(O)}_{1.5}]_{0.65}-$   
During Heating as Characterized by  $^{29}\text{Si}$  Magic Angle  
Spinning NMR.

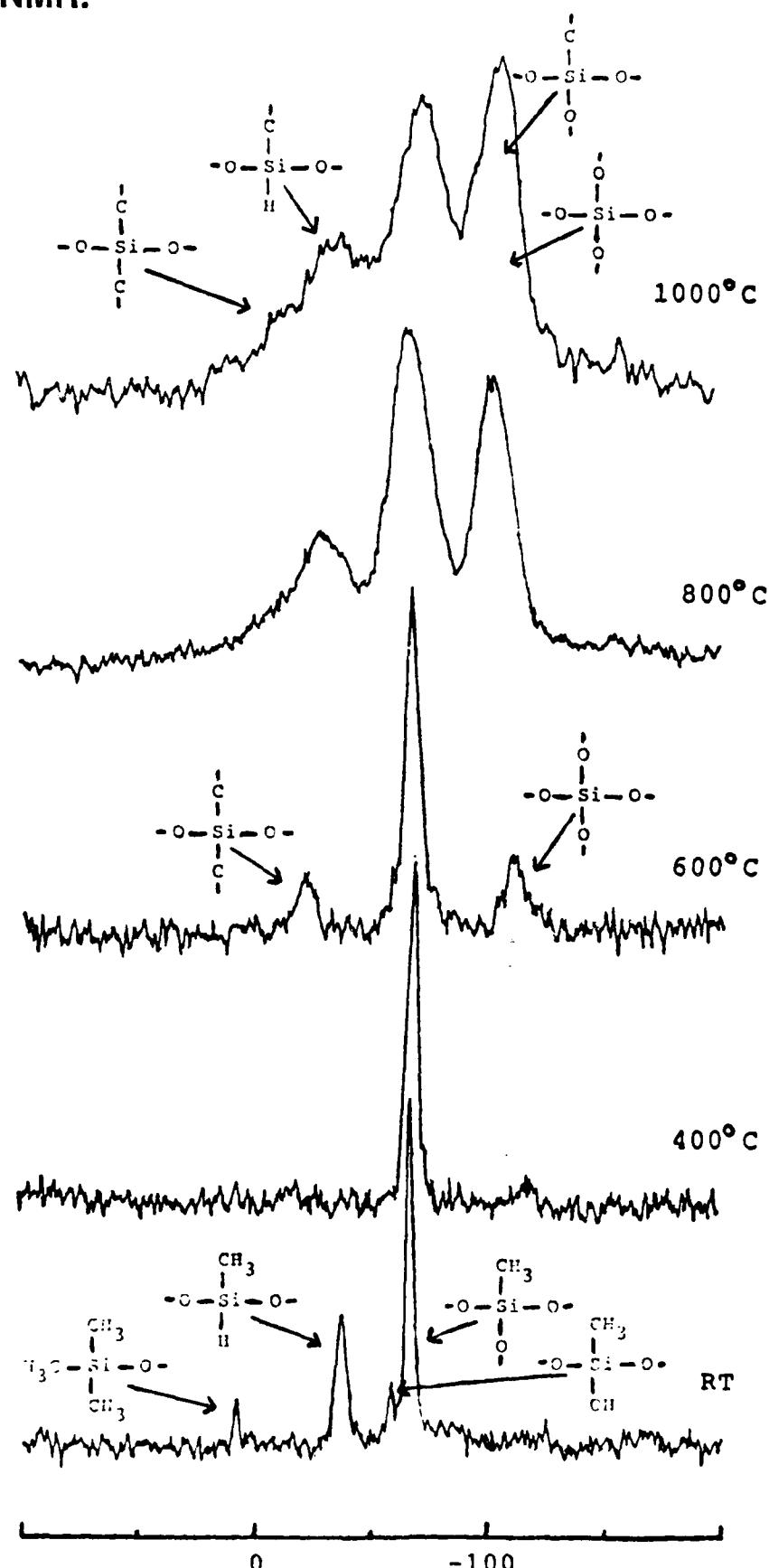


Fig 3

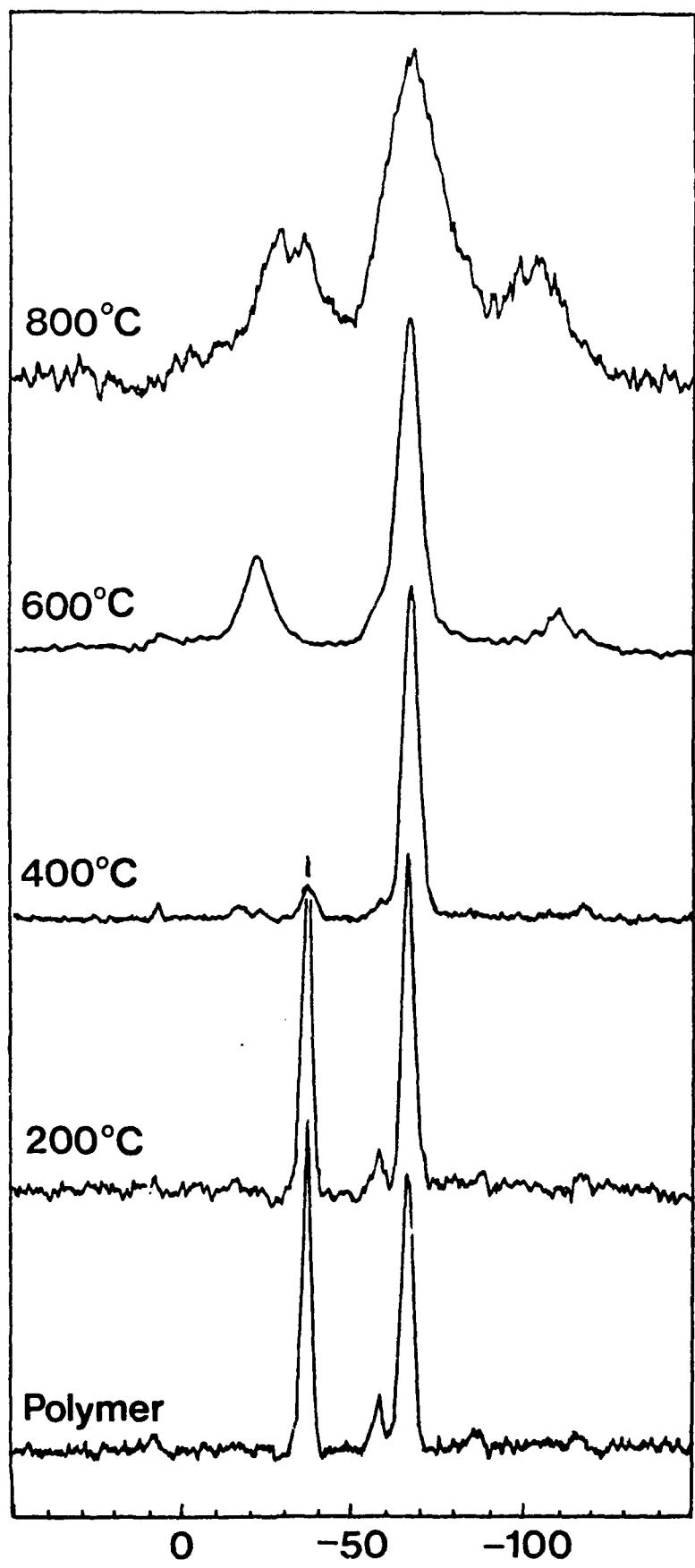


Fig. 4

Chemical Shift (ppm)

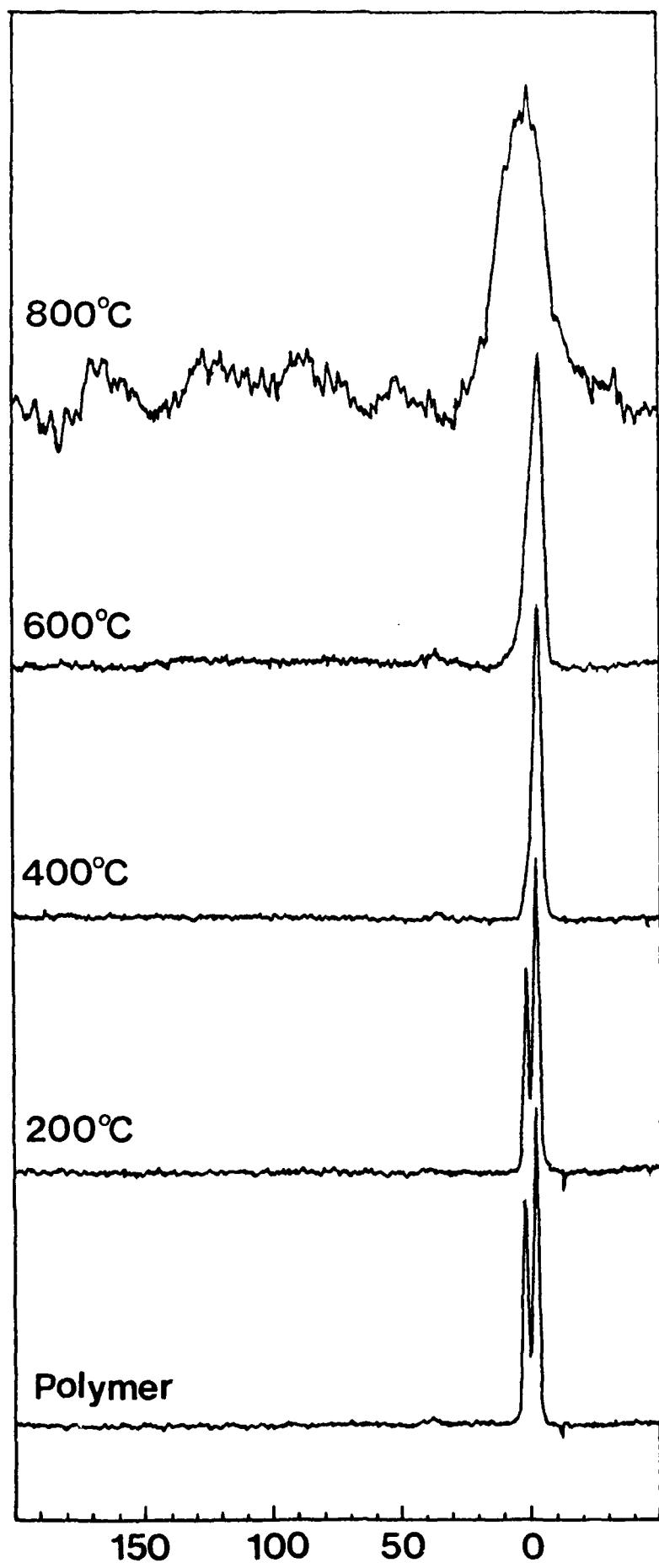


Fig 5

Chemical Shift (ppm)

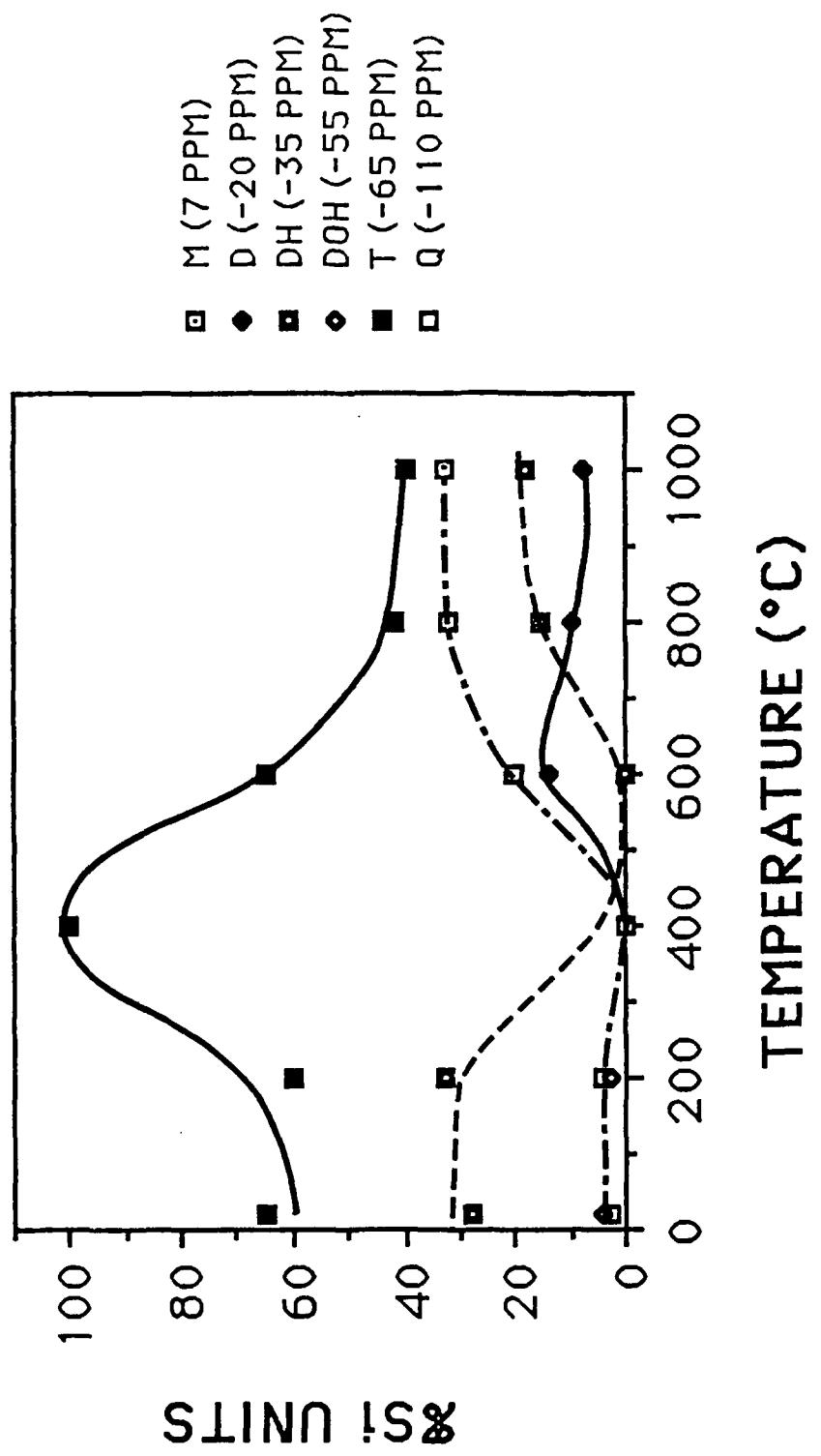


Fig. 6